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Degradation of glycerol using hydrothermal process

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ABSTRACT

Sub-critical or supercritical water was utilized for the degradation of glycerol in an environmentally benign reaction. The reaction was carried out in a batch reactor in the temperature range of 473–673 K, pressure of 30 MPa, and reaction time of 20–60 min. The effects of temperature and reaction time were observed. The degradation of glycerol produced acetaldehyde, acrolein, allyl alcohol and unidentified products. The highest yield of acrolein, acetaldehyde and allyl alcohol were 0.20, 7.17, 96.69 mol%, respectively. Glycerol conversion was 99.92 mol%. While acetaldehyde was formed only in sub-critical water and allyl alcohol only in supercritical water, acrolein was formed in both. The kinetics of the global reaction displayed a pseudo-first-order. The activation energy at subcritical water was 39.6 kJ/mol. Based on the results, this method could be an efficient method for glycerol degradation because the high conversion of glycerol was obtained.

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1. Introduction

Biodiesel production is expected to increase in future with the depletion fossil fuels, leading to an increase in byproducts of biodiesel production, approximately 10% of which is glycerol. However, the glycerol produced from biodiesel still contains many impurities such as water, salts, unreacted alcohol, and unused catalyst (Van Gerpen, 2005). These products can cause serious environmental problems. Glycerol is widely used in various fields such as food, pharmacy, and cosmetics. In foods, glycerol is used as a humectant, solvent, and sweetener. It is also used in medical, pharmaceutical, and personal care preparation, serving as a humectant and a component for improving smoothness and providing lubrication (Yuksel et al., 2010). Although glycerol is an important material, but an excessive amount of glycerol will put downward pressure on its price; thus, its conversion into value added products is of interest. Decomposition of glycerol produces varieties of value added products such as acrolein, acetaldehyde, propionaldehyde, allyl alcohol, methanol, ethanol, formaldehyde (Buhler et al., 2002), lactic acid, formic acid (Yuksel et al., 2009), 1,2-propanediol (Yuan et al., 2010), glycolipids (Liu et al., 2011) gas products, such as hydrogen (Kivistö et al., 2010), syngas (Adhikari et al., 2007) and fuel cell (Nimje et al., 2011).

Water in sub- and supercritical condition has different properties from water at room temperature. The water properties are dependent on temperature and pressure. In the subcritical region, its ion product is higher than in ambient conditions, meaning that it acts as an acid/base catalyst precursor. In a hydrothermal process, water may act not only as a solvent but also as a reactant, catalyst or product (Kruse and Dinjus, 2007). In a supercritical region, water assumes particular properties making it highly reactive and miscible with organic molecules and gases due to its low dielectric constant. Recently, reactions in sub and supercritical water attracted attention from all fields. In biotechnological application, Biller and Ross (2011) conducted hydrothermal liquefaction of microalgae into oil. Protein and lipid could be converted to oil most efficiently without a catalyst. Comparison of different pre-treatment methods for lignocellulosic material included hydrothermal treatment was also carried out by Wörmeyer et al. (2011). They reported that hydrothermal followed by enzymatic hydrolysis produced high quality lignin. Moreover, hydrothermal treatment was completed with dry torrefaction pretreatment on equilibrium moisture content of lignocellulosic biomass by Acharjee et al. (2011). In this case, hydrothermal process produced a more hydrophobic solid than the one produced by dry torrefaction. The application of hydrothermal treatment on the energy production was conducted by Richter et al. (2011). They studied the effect of preconditioning temperature on the energy production from grass silage and reported that the increase in temperature resulted in the increasing combustion quality of the press cake, which was considered as a promising biofuel.

Hydrothermal process has also been widely applied in the degradation of glycerol (Antal et al., 1985; Buhler et al., 2002; May

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et al., 2010; Ott et al., 2006; Ramayya et al., 1987; Watanabe et al., 2007). In the previous studies, glycerol degradation using hydrothermal treatment was carried out in flow process (Buhler et al., 2002; Watanabe et al., 2007) at temperature of 573–748 K, pressure range of 25–45 MPa and reaction time from 9 to 165 s. However, the highest conversion of glycerol reported by Buhler et al. (2002) and Watanabe et al. (2007) were still low, those were 31.38 and 15 mol%, respectively. Glycerol degradation with Ru/ZrO_2 as catalyst using hydrothermal treatment in flow process has also been studied by May et al. (2010) at temperature of 783–823 K, pressure of 35 MPa, and reaction time from 2 to 10 s. They obtained almost complete conversion of glycerol with acetaldehyde as main product and inhibited acrolein. Glycerol degradation in batch process by hydrothermal electrolysis has also been reported by Yuksel et al. (2009). The conversion of glycerol achieved 84 mol% at 553 K with 50 mM NaOH concentration, while the highest yield of lactic acid was 34.7 mol%. As resulted in the previous works, the batch process provided high conversion of glycerol with simple apparatus and long reaction time compared to the flow process. Moreover, the batch process may be carried out without catalyst at longer reaction time to get higher conversion of glycerol. Thus, this paper focuses on the degradation of glycerol using batch process in hydrothermal treatment without catalyst. The effect of temperature and reaction time on the yield of products and glycerol conversion was investigated. This work was expected to produce high conversion of glycerol and value added products.

2. Methods

2.1. Materials

Glycerol with 99% purity, acetaldehyde, acetonitrile, $HClO_4$ and BTB were purchased from Wako Pure Chemical Co., Japan. Acrolein was obtained from Tokyo Chemical Industry Co., Ltd., Japan.

2.2. Methods

The experiments were carried out in a SUS 304 reactor with an inner volume of 8.8 cm^3 (AKICO Co., Ltd., Japan). The loaded amount of glycerol was 0.5 g for all batch experiments and the loaded amount of water depended on the resulting pressure (Span and Wagner, 1996) as can be shown in Table 1.

The reactor containing the sample solution was purged by Argon gases to eliminate air, sealed and was then heated in an electric furnace (ISUZU Co., Ltd., model NMF-13AD). Following the desired time, the reactor was immersed in a water bath to stop the reaction. The liquid product was analyzed by HPLC installed with an ODS-3 Inertsil column using 0.6 ml/min of 20% volume acetonitrile in water. The column was maintained at 30 °C and the volume injected was 20 µl. The analysis was performed using a UV–Vis detector at 210 nm. The chromatograph peaks were identified by comparison of retention time of sample with those of standard compounds without any internal standard. The HPLC chromatogram is provided in the Supplementary Material. The concentration of un-reacted glycerol was analyzed by HPLC with a Sugar SH-1011 column using RI detector. Mobile phase was $HClO_4$ (0.003 M) and BTB (0.1 M) for coloring medium with flow rate of 1 and 0.5 ml/min, respectively. Column temperature was held on 60 °C.

Table 1
Amount of water loaded to the reactor.

Temperature (K)	Mass of water (g)	Pressure (MPa)
473	5.25976	29.55
523	6.76132	29.55
573	6.10000	29.55
623	5.15347	29.55
673	2.46560	29.55

3. Results and discussion

Experiments were carried out under sub- and supercritical water treatment without catalyst in a batch process. Product yield was defined as concentration of product divided by initial concentration of glycerol, while conversion of glycerol was obtained based on initial and residual concentration of glycerol. The identified products were acetaldehyde, acrolein, and allyl alcohol.

3.1. Effect of reaction conditions

Fig. 1 shows the effect of reaction time on acrolein yield at various temperatures. At temperature of 473 and 523 K, acrolein yield gradually increased with increasing reaction time. Increasing the temperature up to 573 K led to a dramatic increase in acrolein yield with increasing reaction time. At this condition, water is under sub-critical condition, where the ion product of water is higher. The ion product of water promotes the ionic reaction that results in the degradation of glycerol into acrolein. It has been explained by Buhler et al. (2002) that acrolein is formed by ionic and radical reaction. Ott et al. (2006) also confirmed that glycerol dehydration in the near sub-critical water follows an ionic mechanism. In contrary, when the temperature was increased to 623 K, or near the critical point of water, the acrolein yield started to decrease at a reaction time of 40 min. At this condition, the degradation of acrolein into other products began. The acrolein might be decomposed into acrylic acid and acrylamide due to the heating (Mestdagh et al., 2008) or into polyacrolein (Ott et al., 2006). Watanabe et al. (2007) has reported in the kinetics model that acrolein decomposed into other products without mentioning their compounds at near critical water, while Ott et al. (2006) also mentioned that without catalyst, consecutive reaction of acrolein occured (e.g. decarbonylation and polymeration of acrolein) and conversion of acrolein achieved 40 mol%. At 673 K, or supercritical condition, and at 20 min of reaction time, a high acrolein yield was obtained. The acrolein yield decreased with increasing reaction time, possibly due to retro aldol reaction occurring in the cooling process. As stated by Antal et al. (1985), acetaldehyde was formed by reverse aldol mechanism from 3-hydroxypropanal and intermediate products, such as acrolein, via homolytic C–C bond cleavage.

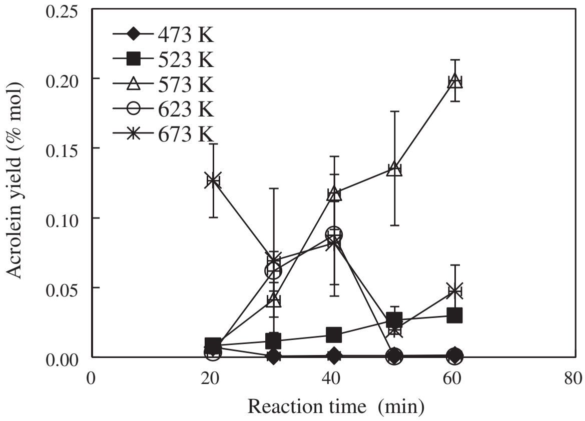

Fig. 1. Acrolein yield as function of reaction time at various temperatures.

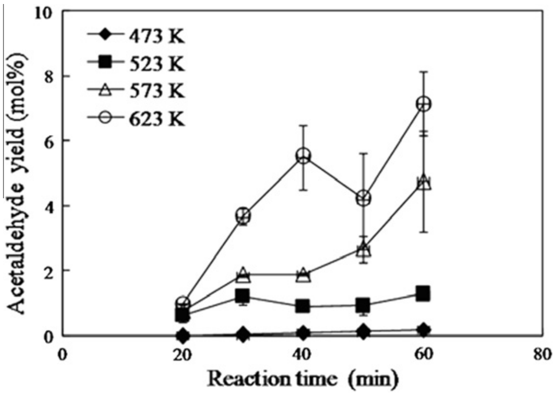

Fig. 2. Acetaldehyde yield as function of reaction time at various temperatures.

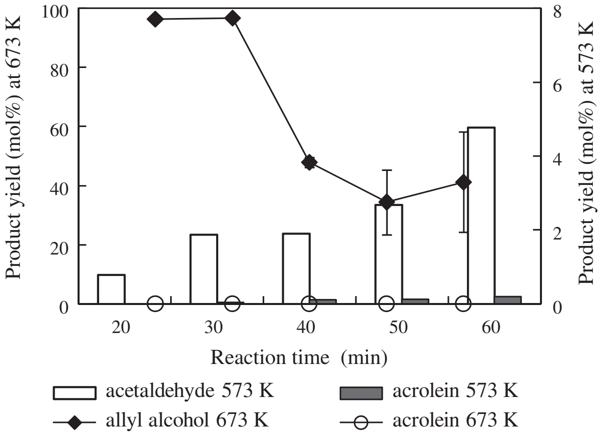

Fig. 3. Product yield as function of reaction time at temperature of 573 and 673 K.

Table 2
Properties of water at experimental condition.

Temperature (K)	Dielectric constant	Ion product (mol/kg)^2	Density (g/ml)
298	78.7	1.00E-14	0.997
473	35.9	7.20E-12	0.655
523	28.3	1.00E-11	0.825
573	21.8	8.20E-12	0.750
623	15.5	2.40E-12	0.642
647	8.8	3.10E-14	0.386
673	5.5	7.00E-16	0.337

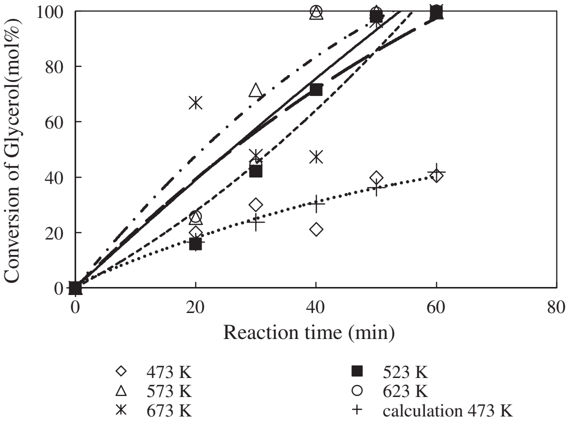

Fig. 4. Conversion of glycerol as function of reaction time at various temperatures.

Fig. 2 shows the influence of the reaction time on acetaldehyde yield at various temperatures. At temperatures of 473 and 523 K, acetaldehyde yield gradually increased with increasing reaction time. Increasing the temperature to 623 K led to a sharp increase in acetaldehyde yield, but at the temperature of 673 K, or supercritical region, acetaldehyde vanished and another product, allyl alcohol, appeared in large quantities as shown in Fig. 3. In Fig. 3, allyl alcohol decreased with increasing reaction time, indicating that allyl alcohol begins to decompose to other products at a reaction time of 40 min. The existence of allyl alcohol at the temperature of 673 K indicates the reaction mechanism changes from sub-critical to supercritical water. Buhler et al. (2002) stated that allyl alcohol is formed only by free radical mechanism, while acetaldehyde and acrolein are formed by an ionic and free radical reaction. The high-temperature water supports either free radical or polar and ionic reactions. The change of the water properties with increasing temperature leads to a change of reaction pathways from ionic to free radical. The properties of water at experimental condition can be seen in Table 2. The ion product, or dissociation constant (K_w) for water as it approaches the critical point, is about 3 orders of magnitude higher than it is for ambient liquid water. Accordingly, in addition to near-critical and supercritical water being an excellent solvent for organic compounds, it can also boost higher H^+ and OH^- ion concentrations than liquid water under certain conditions. In fact, the dissociation of water itself near the critical point generates a sufficiently high H^+ that some acid-catalyzed organic reactions proceed without any added acid. When exceeding the critical point, however, K_w decreases so dramatically that supercritical water becomes a poor medium for ionic chemistry (Savage, 1999). Table 2 also indicates that the dielectric constant decreased with increasing temperature. Hydrogen bonding in water becomes weaker and less persistent with decreasing dielectric constant: a low dielectric constant causes water to behave more like a polar organic solvent than ambient liquid water. Consequently, small organic compounds are highly soluble in high temperature water and completely miscible in supercritical water (Akiya and Savage, 2002). According to properties of water in sub-critical or supercritical conditions, reactions occur by competing ionic and free radical reaction pathways whose predominance depends on water density and its ionic product. In sub-critical water, high ion products provide an opportunity for ionic reactions while in supercritical water, low ion products favor free radical reactions (Buhler et al., 2002).

In addition, Fig. 3 also shows a comparison of acetaldehyde and acrolein yield as a function of reaction time at a temperature of 573 K. The yield of acrolein gradually increased with reaction time, while the yield of acetaldehyde increased sharply; thus, the yield of acetaldehyde was higher than that of acrolein, with the highest acetaldehyde and acrolein yield at 573 K were 7.17 and 0.20 mol%, respectively. Moreover, at 673, the highest acrolein and allyl alcohol yield were 0.12 and 96.69 mol%, respectively. The results indicated that the reaction mechanism followed the mechanism proposed by Buhler et al. (2002), where acetaldehyde and acrolein were produced via an ionic reaction, while allyl alcohol was produced through free radical reactions.

Fig. 4 shows the conversion of glycerol as a function of reaction time at different temperatures. Though the conversion of glycerol was very high, below the temperature of 673 K, the product obtained was small compared to its conversion, a result difficult to explain due to the many unidentified products produced and the negligible production of gas products. The highest glycerol conversion was 99.92 mol% at temperature of 623 K and reaction time of

Table 3
Comparison between different studies of glycerol degradation by hydrothermal process.

Author	Conversion of glycerol	Process
Ramayya et al. (1987)	6% (573 K, 34.5 MPa, 16 s)	Flow
Ott et al. (2006)	80% (633 K, 34 MPa, 60 s with 790 ppm of zinc sulfate as catalyst)	Flow
Buhler et al. (2002)	31.38 mol% (740 K, 450 MPa, 98.1 s)	Flow
Watanabe et al. (2007)	15 mol% (673 K, 34.5 MPa, 21 s)	Flow
Yuksel et al. (2009)	84% (553 K, 10 MPa, 2A, 90 min)	Hydrothermal electrolysis, batch
Yuksel et al. (2010)	93% (1A, 90 min)	Hydrothermal electrolysis, flow
May et al. (2010)	Almost complete conversion (823 K, 35 MPa, 8 s with 1% of Ru/ZrO_2 as catalyst)	Flow

Table 4
Reaction rate constant at certain temperature.

Temperature (K)	k (min^{-1})
473	0.009
523	0.065
573	0.095
623	0.106
673	0.073

60 min. Fig. 4 also shows a comparison of experimental and calculated conversion at a temperature of 473 K. The range of deviation standard was 0–1.96. It indicated that pseudo-first-order approximation was appropriate with the experimental result.

Table 3 shows comparison between different studies of glycerol degradation by hydrothermal process. All previous work without catalyst indicated low conversion (3–31.38%), whereas with catalyst indicated high conversion (80–100%), but this work showed high conversion of glycerol without catalyst. Actually, this work agrees with the previous works, however the reaction time caused the different results. In addition, hydrothermal treatment in batch process provides longer residence or reaction time to complete the degradation without catalyst. Compared with the previous works, most of the experiments were conducted in short reaction/residence time in flow process with and without catalyst. Moreover, the reaction with electrolysis in hydrothermal condition also resulted in high conversion due to the assistance of electric and electrolyte for reaction.

3.2. Kinetic analysis

Kinetic analysis for glycerol degradation was conducted based on data for a reaction time of 20–60 min and in a temperature range of 473–673 K. The mechanism of glycerol degradation was complicated by the many unidentified products, so simplifications were made to determine the kinetics equation. The kinetic equation was calculated based on the initial and remaining concentrations of glycerol. The overall rate reaction was described by pseudo-first-order kinetics due to the two reactants, but the amount of water was excessive can be expressed in the following forms:

$$\text{Glycerol} + \text{Water} \Rightarrow \text{products}$$

Reaction rate:

$$\frac{\mathrm{d}C_A}{\mathrm{d}t} = k_1 C_A{}^a C_B^b \tag{1}$$

$$\frac{\mathrm{d}C_A}{\mathrm{d}t} = k_1' C_A^a \tag{2}$$

Here k_1 is kinetic constants of glycerol consumption, k_1' is k_1 $[C_B]^b$, and C_A and C_B are the concentration of glycerol and water, respectively. The rate constant, k, determined from Eq. (2) can be seen in Table 4. It shows that below critical temperatures, the reaction rate increased with increasing reaction time; conversely, in supercritical regions, the reaction rate decreased with the reaction time. Ott et al., 2006 explained that reaction rate decreased in supercritical water because the self-dissociation of water decreases. It also indicated that other mechanism reaction, e.g. free radical, dominated in supercritical water (Buhler et al., 2002).

The activation energy in sub-critical water was 39.6 kJ/mol determined from Arrhenius equation; unfortunately, the activation energy cannot be determined in supercritical water because reaction in supercritical condition was carried out at one temperature condition.

4. Conclusions

Degradation of glycerol was studied by hydrothermal process at 30 MPa, a temperature range of 473–673 K, and a reaction time of 20–60 min. Products of glycerol degradation were acetaldehyde, acrolein, allyl alcohol, and other un-identified products. The highest yield of acrolein, acetaldehyde and allyl alcohol, and glycerol conversion were 0.20, 7.17, 96.69, 99.92 mol%, respectively. In subcritical water, the products were acetaldehyde and acrolein; in supercritical water, they were allyl alcohol and acrolein. The overall reaction rate was described by pseudo-first-order kinetics, and the activation energy of reaction was 39.6 kJ/mol in subcritical water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2011.06.066.

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